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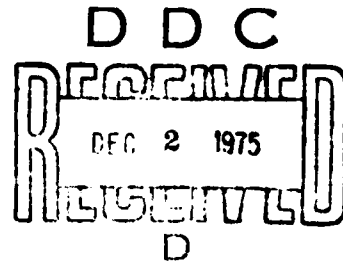
THE CORROSION OF ST-4 STEEL IN THE NATURAL
ATMOSPHERE AND THE CORRELATION OF THE RESULTS
WITH THE RESEARCH IN THE AEROSOL CHAMBER

by

K. Szawlowska-Wallisich and Z. Zurek



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By: K. Szawlowska-Wallisch and Z. Zurek

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THE CORROSION OF ST-4 STEEL IN THE NATURAL ATMOSPHERE AND THE
CORRELATION OF THE RESULTS WITH THE
RESEARCH IN THE AEROSOL CHAMBER

Krystyna Szawlowska-Wallis and Zbigniew Zurek

The results of the research carried out by accelerated methods, in general, do not represent the best data as they cannot be attributed to the conditions of the normal utilization of metal and, on that basis, the durability of metal in the natural atmosphere cannot be determined. That possibility merely establishes the determination of the appropriate conversion coefficients which characterize the magnitude of the acceleration in the results of the accelerated laboratory test as compared to the findings in the natural atmospheric conditions.

The objective of the present work was the investigation of the rate of corrosion of ST-4 steel in various natural atmospheres: urban-industrial, laboratory and room atmosphere, as well as the calculation of the correlation coefficients, in comparison with the accelerated methods in an aerosol chamber with vapors of NaCl solution [1] and with vapors of H_2O at room temperature $20 \pm 1^\circ C$.

Specimens in all the investigated environments are exposed to the action of the agents found in the atmosphere for a period of 12 months. During that period they are subjected to observations; the quantity of the weight loss of the investigated specimen or, in the case of the corrosion in the room atmosphere, the quantity of the mass increase is determined in specified time intervals (1,2,3,6,9, and 12 months).

In the case of the investigation in the urban atmosphere, meteorological conditions such as temperature, humidity, atmospheric precipitation, direction of wind and its velocity have played important roles. The frequency of changes of the intensity of the individual elements, particularly temperature and humidity, are also of considerable importance during daytime. Besides the meteorological factors, the corrosion of steel to a large extent is caused by atmospheric pollution resulting from house fumes, which are present in the vicinity of production plants as well as transportation facilities. In the urban atmosphere, impurities can be found such as sulphur oxides, nitrate oxides, carbon monoxide, and dust. Corrosion in such environments is greatly diffused and the majority of the steel constructions utilized in the open air is subject to destruction due to the water vapor in the air condensing on their surfaces. This corrosion is of an electrochemical character, and in the majority of cases, these corrosive processes proceed from oxygen depolarization. The condensed water vapor attracts CO_2 , O_2 and other aggressive agents which are present in a polluted atmosphere, from the air onto the metal surface. That activity further intensifies the process of corrosion, which can take place in the acid environment from the hydrogen depolarization. These processes take place in a thin layer formed on the metal surface. This thin layer does not constitute a serious obstruction for the diffusion of oxygen; an intensive oxygen depolarization of the cathodic portions of the metal occurs here. On the other hand, as was demonstrated in the works of Tomaszow [2], the probability of the formation of anodic passivity increases in connection with the easy access of the oxygen onto the surface of the metal. In connection with that fact, it can be assumed that in humid air, two kinds of phenomena can occur; namely, the activation of the cathodic process and repression of the anodic process of the metal ionization. Theoretical considerations and research [3] on the topic of the humidity alone led to the drawing of the conclusion that rusting in clean air with relative humidity below 100% is hardly observable. However, a sudden increase in the rate of corrosion is observed at a certain critical relative humidity; this is caused by the fact that a thin layer of electrolyte is created on the metal surface. Rosenfeld dealt with the problem of thin layer corrosion. He discovered that the

factor which determines the rate of metal destruction is the oxygen dissolved in the thin layer, and that the process of corrosion depends on the cathodic reduction of oxygen. The rate of the oxygen reduction depends on the thickness of the diffusion layer d , coefficient of corrosion δ , and concentration of oxygen c , the magnitude can be described by a mathematical formula

$$i = \frac{d \cdot n \cdot F \cdot c}{\delta}$$

where

i - current density

F - Faraday constant

n - number of electrons participating in the process of a discharge of one oxygen molecule

Based on the formula, we can conclude whether the process of the oxygen cathodic reduction is controlled by diffusion. On the basis of calculations, Rosenfeld came to the conclusion that the rate of the oxygen reduction is considerably higher than would be expected from theoretical considerations. This can be explained by the fact that besides diffusion in the thin layers, the self-mixing and convection of oxygen take place as well. When investigating the process of oxygen depolarization in the thin layers of electrolyte, Rosenfeld confirmed a curious phenomenon consisting of a distinct increase in the speed of oxygen depolarization in the case of the evaporation of the electrolyte from the metal surface. In the process of rusting, in the first stage we are concerned with the formation of the iron hydroxide and subsequent series of reactions among the oxide, products of corrosion and water.

The final product is rust composed of $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$. This is a simplified outline of reactions taking place. It is necessary to remember that the process of corrosion of steel is very complex.


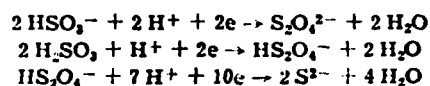


Photo 1. Photo of the surface of corroded ST-4 steel affected by corrosion in urban environmental conditions.

When investigating specimens in the urban atmosphere, relative humidity of the air is subjected to numerous changes, depending on the quantity of rainfall or snowfall. Besides humidity, the degree of atmospheric pollution has a great influence on the rate of steel corrosion in the urban atmosphere, and depending on these conditions, the rate of corrosion can change.

Aggressive gas impurities are dissolved in the humid air and in the atmospheric precipitation, they pass into solutions of acids, alkali, and salt, which constitute a large threat to steel constructions. The vigorous activity of SO_2 is usually accompanied by changes in the pH of the environment, leading to the destruction of the protective layer. Under favorable conditions, SO_2 oxidizes into SO_3 , which, after being dissolved in water, produces sulphurous acid. SO_2 acts as a cathodic depolarizator, accelerating the cathodic processes several times.

The solubility of SO_2 in the thin layers of the electrolyte is higher than the solubility of oxygen, and therefore, the concentration of SO_2 is greater. On the basis of the thermodynamic calculations and polarographical investigations, scientists [4] have proposed several mechanisms:



Products of the reactions (HS_2O_4^- , $\text{S}_2\text{O}_4^{2-}$, S^{2-}) resulting as the consequence of the cathodic reaction can undergo further changes.

In industrial centers rain water can contain up to 0.01% of H_2SO_4 .

The increase of humidity in the atmosphere, even with small contents of SO_2 , results in strong corrosion of carbonic steel in particular [5]. Impurities of steel present on the metal surface, such as dust, soot, sand, etc., also cause the acceleration of the corrosive process. They can establish cores of the capillary condensation of the water vapor, which, in contact with steel, can also have a harmful effect. Corrosion of steel progresses considerably faster in the spring rainy season than in the summer months, independently of lower temperatures. Temperature fluctuation is also a great influence. In less polluted environments carbon dioxide, which is always present in the air, increases electrical conductivity and acidity of moisture. Its direct corrosive activity is not large compared to SO_2 and chlorides. In some cases the carbon dioxide can inhibit the process of steel corrosion. The rate of metal destruction caused by chlorides is relatively important [1], this phenomenon exists only above the ocean where the waves crashing at the shore give rise to the sea water aerosol.

Temperature of the environment certainly plays a role as a factor accelerating the rate of the metal corrosion, nevertheless, it is assumed that the fundamental influence is not determined by the

average temperature, but by the fluctuations of temperature which cause evaporation or condensation of moisture. The sudden changes in the temperature also influence to a large extent the rate of the reaction between SO_2 and steel. Photo 1 represents an illustration of corroded steel affected by corrosion under urban environmental conditions.

Microscopic observations indicate that corrosion of steel in such cases has the character of an "eating" corrosion.

Laboratory atmosphere certainly differs from urban atmosphere by the amount of moisture in the air. Pollution by various aggressive elements such as NH_3 , SO_2 , CO_2 , chlorides, and nitrate oxides greatly affects steel corrosion. Here, the corrosion process is considerably slower; relative humidity in the laboratory atmosphere amounts to less than 100%.

Corrosion in the room atmosphere deprived of aggressive elements but containing O_2 , CO_2 can be considered as a "dry" corrosion; here, the condensation of a layer of moisture on the steel surface does not occur. A loss of surface gloss is observed, which is caused by the formation of the products of chemical corrosion. The thickness of the layer slowly increases and this corrosion type can transform into a "wet" corrosion. In Table 1, the constants of the corrosion rate in investigated environments are assembled.

TABLE 1. CONSTANTS OF THE CORROSION RATE OF ST-4 STEEL IN NATURAL ENVIRONMENTAL CONDITIONS IN g/cm^2 MONTH

Month	Room atmosphere	Laboratory atmosphere	Urban atmosphere
1	$2.42 \cdot 10^{-6}$	$1.75 \cdot 10^{-6}$	$1.28 \cdot 10^{-2}$
2	$2.42 \cdot 10^{-6}$	$5.11 \cdot 10^{-6}$	$1.33 \cdot 10^{-2}$
3	$1.03 \cdot 10^{-5}$	$1.14 \cdot 10^{-5}$	$1.85 \cdot 10^{-2}$
6	$6.99 \cdot 10^{-5}$	$2.17 \cdot 10^{-5}$	$3.79 \cdot 10^{-2}$
9	$7.13 \cdot 10^{-5}$	$2.86 \cdot 10^{-4}$	$4.89 \cdot 10^{-2}$
12	$1.19 \cdot 10^{-4}$	$1.36 \cdot 10^{-3}$	$7.93 \cdot 10^{-2}$

TABLE 2. CONSTANTS OF THE CORROSION RATE OF ST-4 STEEL IN
VARIOUS ENVIRONMENTS IN g/cm^2 HOUR

Room atmosphere	Laboratory atmosphere	Urban atmosphere	Mist of solution 3% NaCl pH = 3	Mist H_2O
$3.47 \cdot 10^{-10}$	$8.3 \cdot 10^{-10}$	$1.47 \cdot 10^{-6}$	$2.35 \cdot 10^{-5}$	$1.62 \cdot 10^{-6}$

On the basis of the conducted experiments it is observed that corrosion processes run faster in natural atmospheric conditions, and considerably slower in the laboratory and room atmosphere. Comparing the obtained results with the results of investigations obtained by the accelerated method in the aerosol corrosive chamber with the dispersion of 3% of NaCl with a pH of 3 [1], it is confirmed that the acceleration with reference to the laboratory investigations conducted in the urban atmosphere amounts to 16, in the laboratory atmosphere 28,300, and in the room atmosphere 67,700. In comparison with the investigations in an aerosol chamber in which H_2O is dispersed, the coefficient of acceleration is smaller; for urban atmosphere it amounts to 1.1, for laboratory atmosphere - 1,950, and for room atmosphere 4,670. Considerably higher acceleration coefficient for dispersion of NaCl solution with pH = 3 is connected with the aggressive activity of chloride ions and with the acidic environment.

The above experiments were conducted in Krakow in the middle of an industrial center, near to a foundry, railway, and a main communication artery. The calculated correlation coefficient is characteristic for the investigated center; it can be admitted that its value will be different for other industrial centers depending on their pollution.